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(54) Title: METHOD FOR PRODUCING DIETARY FIBERS FROM NONWOODY LIGNOCELLULOSIC SUBSTRATES BY OXIDATION		
(57) Abstract <p>A process for delignifying and optionally bleaching nonwoody lignocellulosic substrates to produce a dietary fiber suitable for human consumption is disclosed. The process involves (a) an optional first step of treating the substrate with an aqueous alkali solution containing 1 to 20 % by weight, based on dry substrate, of a base at 20° to 100 °C to swell and remove base soluble materials from the substrate; (b) separating the substrate and optionally washing it with water; (c) uniformly wetting the substrate with an aqueous alkaline solution containing 1 to 20 wt. % of base, based on dry substrate, to form a slurry, placing the slurry in a pressure vessel which is pressured with oxygen gas to 20 to 300 psig (138 to 2070 kPa) for 5 to 180 minutes at a temperature of 50° to 150 °C to delignify the substrate, separating the delignified substrate from the lignin containing extract solution; (d) optionally bleaching the delignified substrate, preferably with an alkaline aqueous hydrogen peroxide solution; and (e) recovering the delignified substrate. Optionally more than one oxygenation step can be used with the substrate being separated from the oxygenation-extraction medium between oxygenation steps. Optionally, in a preferred aspect of the present invention a peroxide, preferably 0.5 to 10 weight percent hydrogen peroxide, is included in the reaction medium during one of the oxygenation steps.</p>		

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TITLEMETHOD FOR PRODUCING DIETARY FIBERS FROM
NONWOODY LIGNOCELLULOSIC SUBSTRATES BY OXIDATION

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BACKGROUND OF THE INVENTION

The present invention relates to delignifying and optionally bleaching nonwoody lignocellulosic substrates, and, more particularly to delignifying of nonwoody lignocellulosic substrates using O_2 which converts the substrate into a source of dietary fiber suitable for human consumption which has a high brightness level, i.e., in most cases having a brightness level in the range of above 85 and preferably 90 or higher, and a total dietary fiber content of usually over 90% by wt. and a high water and oil absorbency. A low calorie dietary fiber of the type which can be prepared according to this invention can also be characterized as having a low content of proteinaceous, fatty and ash-forming materials, such that it can be substituted for farinaceous flour at high replacement levels, a binding agent for processed meat, and partial replacement for fat and sugar, or bland fiber for fiber drinks, as well as pharmaceutical use.

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SUMMARY OF THE INVENTION

The present invention is a method for delignifying, i.e., converting nonwoody lignocellulosic agricultural residues into a source of dietary fiber which is suitable for human consumption and has a total dietary fiber (TDF) content of generally above about 90% by weight which comprises:

- 25 (a) optionally uniformly wetting the residue, i.e., the substrate, with aqueous alkali having a concentration in the range of from 1% to 20% by weight, based on dry substrate, at a temperature in the range of from 20° to 100° C to swell and remove base soluble materials from the substrate;
- (b) optionally separating the substrate from the aqueous alkali and washing it with water;
- 30 (c) uniformly wetting the substrate with an aqueous alkaline solution containing 1-20 wt.% base, based on dry solids present, while pressuring the substrate at from 20 to 300 psig (138 to 2070 kPa) with O_2 gas at a temperature of 50° to 150° C for 5 to 180 minutes optionally in the presence of peroxide to reduce
- 35 lignin content and improve brightness, and separating the substrate from the extract liquid;

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(d) optionally repeating the O_2 treatment step after separating the substrate from the extraction liquid, this two-stage process provides a product with considerably improved brightness;

(e) optionally uniformly wetting the substrate with a bleach such as aqueous alkaline hydrogen peroxide having a concentration of from about 0.5% to about 10% by wt. peroxide based on the original dry weight of the substrate at 20° to 100° C for 30 minutes to 6 hours;

(f) acidifying the substrate to pH 2-3 to remove residual base and ash, and then washing; and

(g) recovering the delignified fiber.

The process of the invention produces bleached cellulosic fiber products having a brightness level which for practically all cases exceeds 85 and preferably is above 90 and which have a total dietary fiber content generally above 90% by weight. In addition, the bleached products are substantially free of nutritive proteinaceous, carbohydrates and fatty components and ash-forming, especially siliceous, components. The fiber products of the invention can be used as farinaceous flour substitutes in replacement concentrations exceeding 20 percent by weight of the flour, as well as in dietary fiber drinks, pharmaceutical uses and bulk extenders for artificial sweeteners and fats.

By maintaining the temperature of the O_2 treatment process range of from 50° C to about 150° C and preferably 90° to 130° C, the process improves brightness levels of the product, reduces lignin, and reduces the content of fats, oil and protein to acceptable levels. Low calorie dietary fiber that can be used in high replacement concentrations as a flour substitute can be made from nonwoody agricultural residues according to the process of the invention. Foods made from the resulting flour have good aroma, texture and mouth feel. The process of this invention is particularly effective for treating substrates selected from the group consisting of grain hulls, e.g., oat hulls, peanut hulls, pea hulls, barley hulls, rice hulls, bagasse, soy bean hulls, corn cob chaff and sugar beet pulp. Grain brans such as corn bran, oat bran and wheat brans are especially preferred.

According to one aspect of the invention, the substrate can be optionally uniformly wetted with aqueous alkali by forming a slurry having an alkali concentration of from 1% to 20 % by wt., based on the original dry weight of the substrate, and a consistency of from 5% to 35% and maintaining the substrate in the slurry until the substrate is uniformly wetted, e.g., from about 5 minutes to several hours. Then the substrate is treated with O_2 at a pressure of 20 to 300 psig (138 to

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2070 kPa) and preferably 50 to 200 psig (344 to 1380 kPa), a temperature of 50° to 150° and preferably 90° to 130° C for 5 to 180 minutes and preferably 30 to 90 minutes. One or more O₂ treatment steps may be used. Optionally a peroxide can be present in the oxygenation step(s) to improve brightness.

5 Thereafter, a bleach such as hydrogen peroxide, hypochlorite, chlorine dioxide, ozone, peracetic acid or Cl₂ can be added directly to the slurry containing the substrate to accomplish bleaching after separating the substrate from the slurry. Silica, protein, carbohydrates and fat which have solubilized in the slurry remain behind when the substrate is removed, and since they represent BOD, i.e., biological
10 oxygen demand, as an element of aqueous waste, can be removed through anerobic waste treatment.

DETAILED DESCRIPTION OF THE INVENTION

The invention is an effective delignification and bleaching method for
15 converting a nonwoody lignocellulosic material into a source of dietary fiber for human consumption. The process comprises the following steps:

- (a) optionally uniformly wetting the residue, i.e., the substrate, with aqueous alkali having a concentration in the range of from 1% to 20% by wt. based on dry substrate solids and at a temperature in the range of from about 20° to
20 100° C to swell and remove alkali solubles from the substrate;
- (b) separating the substrate from the slurry and optionally, washing it with water;
- (c) uniformly wetting the substrate with an aqueous alkaline solution containing 1 to 20 wt.% base, based on the original dry weight of the substrate, at an
25 O₂ pressure of 20 to 300 psig (138 to 2070 kPa) and preferably 50 to 200 psig (344 to 1380 kPa); a temperature of 50° to 150° C and preferably 90° to 130° C for 5 to 180 minutes and preferably 30 to 90 minutes, optionally more than one oxygenation step can be used and peroxide can be present in the oxygenation step;
- (d) optionally uniformly wetting the substrate with an aqueous
30 alkaline bleach such as hydrogen peroxide having a concentration of from about 0.5% to about 10% by wt. peroxide based on the dry weight of the substrate;
- (e) acidifying the product to pH 2-3 for 5 minutes to 2 hours, washing to pH greater than 5; and
- (f) recovering the substrate.

35 The recovered substrate is a substantially bleached cellulosic fiber having a TDF of generally over 90% and a greatly enhanced brightness level.

For human dietary fiber products, nutritive proteins, carbohydrates, fats, oils and ash-formers, e.g., silica, are undesirable, and their concentrations in the final treated product must achieve acceptable levels. These levels are not especially critical and can be adjusted by varying the concentrations of alkali, e.g., NaOH, and O₂ employed in carrying out the process. The nutritive content of practically all the substrates must be reduced during processing if the bleached product is to qualify as high "dietary" fiber, that is, as a low calorie or non-fattening food. Reducing fats, particularly unsaturated fats, is needed to avoid objectionable aroma and rancid taste in baked goods. Reducing ash-forming substances is needed to avoid objectionable mouth feel (gritty taste and texture) in baked goods. Reducing lignin eliminates color and gritty texture and increases the water and oil absorbency of the product which imparts a smooth texture to foods incorporating the product.

A preferred class of substrates for use herein are fruits, roots and tubers. The terms "fruits", "roots" and "tubers" are used herein in the botanical sense. Thus, "fruit" is defined as the ripened plant ovary (or group of ovaries) containing the seeds, together with any adjacent parts that may be fused with it at maturity. It is intended that the term "fruit" include simple dry fruits (follicles, legumes, capsules, achenes, grains, samaras and nuts), simple fleshy fruits (berries, drupes, false berries and pomes), aggregate fruits and multiple fruits, as botanically defined. For the purposes herein, the term "fruits" is also intended to include any residual or modified leaf and flower parts which may contain or be attached to the true fruit, such as a bract.

Encompassed within this definition of "fruit" are cereal grains and other seeds. Components of these materials contemplated for use herein include bran and certain seed hulls. "Bran" is a component of cereals and is defined as a fraction obtained during the processing of cereal grain seeds and consisting of the lignocellulosic seedcoat separated from the flour or meal. Examples of nonwoody seed hulls are the bracts of oats and rice. "Root" is defined as the usually underground portion of a plant body that functions as an organ of absorption, aeration and food storage or as a means of anchorage and support, and differs from the stem especially in lacking nodes, buds and leaves. "Tuber" is defined as a much enlarged portion of a subterranean stem (stolon) provided with buds on the sides and tips.

The lignocellulosic substrates of principal interest are waste stream components from commercial processing of crop materials such as sugar beet pulp, citrus fruit pulp, nonwoody seed hulls and cereal bran. Unless otherwise specified,

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the terms "citrus pulp" or "citrus fruit pulp" will be used herein in the generic sense to define the waste product of the citrus juice industry. This product typically includes both the rind of the fruit and also the fleshy juice sacs. The fleshy material is oftentimes also referred to as "pulp", and it alone is a suitable substrate within the
5 ambit of the invention.

The process of the invention is particularly applicable for converting grain hulls into a low calorie dietary fiber. Of the grain hulls, oat hulls are a preferred substrate from which a low-calorie flour substitute can be made because of the general public acceptance of oats in particular as health food for humans.
10 The process of this invention, however, is applicable to a variety of agricultural substrates, such as, for example, substrates selected from the group consisting of bagasse, soy bean hulls, rice hulls, peanut hulls, wheat straw, corn residues such as corn cob chaff, corn bran and corn husks, wheat bran and wheat straw and sugar beet pulp. For convenience, the substrate may be used as it comes from the field;
15 however, more consistent and better results have been observed when the substrate is processed through one or more preparatory steps.

However, nonwoody substrates of the type described in the prior art can differ substantially in composition. Nonwoody materials, for example, have a relatively low lignin content in the range of about 17%, while the lignin content of
20 woody substrates can range as high as 20-35%. Even among a group of nonwoody substrates, substantial differences have been noted from one substrate to another, for example, in mineral content, heavy metal ion content, and in the presence or absence of proteins and fats. In grain hulls, e.g., oat hulls, the presence of silica, protein and fats insofar as their ultimate use as a dietary fiber is concerned is
25 undesirable. Thus, removal of these constituents during delignification can be critical in whether the fiber product which results can be used as a white and bland food additive.

For example, the substrate to be treated is preferably cleaned first by washing with water or by steam washing to remove foreign matter and debris.

30 For best results the substrate is comminuted, i.e., chopped, shredded or ground, to increase its surface area and facilitate handling and wetting with alkali. Grinding the substrate too fine, e.g., less than 100 mesh, should be avoided, however, since filtration, handling and/or drying problems may result along with an increased yield loss. Comminuted substrates tend to yield brighter bleached
35 products if residual liquid can be effectively removed from the substrate, but when the substrate is ground too fine, high efficiency separation, such as, for example, by

centrifugation, is needed to effectively remove liquid.

An optional first step in the process of this invention is to uniformly wet the substrate with aqueous alkali. Wetting can be accomplished by any convenient means, but, preferably, it is accomplished by forming a slurry of the substrate in aqueous alkali and maintaining the slurry for a sufficient length of time and at a temperature in the range of from 20° to 100° C to insure uniform wetting. Preferably, the substrate is first slurried in water and then alkali is added as a concentrated aqueous solution to achieve an alkali concentration in the slurry which can range from about 1% to 20 % by weight, based on original dry weight of substrate.

The alkali is an alkali metal base, such as a hydroxide or carbonate of sodium or potassium, calcium hydroxide, magnesium hydroxide or ammonium hydroxide although NaOH is preferred for convenience and economy. The alkali or its concentrated solution (40-50 weight %) can be added to the aqueous slurry of the substrate all at one or in increments, as desired. If a base other than NaOH is used, it should be present in a molar equivalent to the weight ranges set forth for NaOH.

The consistency of the slurry (weight percent dry substrate in the slurry) is not critical. Preferred consistencies are from about 5% to about 35%. In general, higher consistencies may be employed if the substrate is comminuted.

Uniform wetting of the slurry can be accomplished with conventional blending equipment, such as a pipeline mixer, a blender, an agitated vessel or with recirculating pumps. Full and uniform wetting is indicated when the substrate becomes evenly dispersed and non-buoyant in the slurry.

The temperature for alkalizing the substrate can vary broadly, say, from about 20° to about 100° C. The duration of this alkalizing phase may range from a few minutes to an hour or more depending on the temperature and mixing efficiency. In general, the higher the temperature the shorter the time of treatment required. If a high efficiency mixer, such as a blender, is used, uniform wetting of the substrate can be accomplished in a shorter time period.

Upon completion of the alkalizing phase, i.e., when the substrate has been uniformly wetted with aqueous alkali to swell and hydrophilize the substrate, and solubilize protein, fat, acetyl groups and ash, the substrate is treated with oxygen gas. The swelling of the substrate and solubilizing of protein serves to increase the oxygen permeability of the substrate. If the alkali extraction is used, the substrate should be filtered to remove the alkali extract and the substrate reslurried with water and 1 to 20 weight percent base (based on the weight of oven

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dried substrate). Generally, the aqueous slurry will contain from 5 to 35 weight percent substrate. The aqueous slurry is then sealed in a pressure vessel which is evacuated and then pressured with O₂ to 20 to 300 psig (138 to 2070 kPa) and preferably 50 to 200 psig (344 to 1380 kPa). The sealed pressure vessel is then
5 heated to 50° to 150° C and preferably 70° to 130° C for from 5 to 180 minutes and preferably 30 to 90 minutes.

In a preferred embodiment of the invention the uniformly wetted substrate is separated from the alkalinizing phase, i.e., slurry, by any convenient means and then optionally washed with water before being treated with oxygen.
10 Silica, fat, protein and carbohydrate which have been solubilized in the aqueous alkali remain behind and can be removed from the process. Since they collectively comprise a waste material which generates BOD, the waste can be anaerobically treated.

More than one oxygenation step may be used. If this is done, the
15 substrate should be separated from the extraction after each oxygenation step prior to the succeeding oxygenation step. This is conveniently done by filtration or centrifugation. Optionally the substrate is washed with water after the separation step. The conditions used in the succeeding oxygenation steps are the same as those described herein for the first oxygenation step. The use of two oxygenation steps is
20 preferred and results in a product having considerably improved mouth feel and color.

In another preferred aspect of the present invention, peroxide is present in at least one of the oxygenation steps. Generally from 0.5 to 10 weight percent, based on the dry substrate, is used. This results in a product having
25 considerably improved color and generally eliminates the need for a subsequent treatment with a bleaching agent as described below. Generally hydrogen peroxide is the preferred peroxide and it is simply included in the oxygenation medium described above. Other peroxides or peroxy acids, or their salts, can also be used but their use is not preferred due to the additional expense involved, and, in certain
30 instances, the pH balance problems associated therewith. Preferably, a peroxide stabilizer, such sodium silicate, magnesium sulfate, or sodium tripolyphosphate, is used to enhance product brightness.

The alkaline medium separated from any of the oxygenation steps can be recycled back to the beginning of the process and used to perform the alkaline
35 pretreatment of the nonwoody cellulosic prior to the first oxygenation step.

After the oxygen treatment the substrate is preferably treated with a

bleaching agent. Alkaline hydrogen peroxide is the preferred bleaching agent. The peroxide which can be used according to the process of the invention may be any water-soluble peroxide, such as hydrogen peroxide, hydroperoxide anion HO_2^- and peroxy acids such as peroxyacetic acid and monoperoxy sulfuric acid. H_2O_2 is preferred for its ready availability as a concentrated aqueous solution, 35-70% by weight, and its ease of handling. If other than hydrogen peroxide is used, the total amount of alkali needed should be adjusted to account for the "alkali" content of the peroxide.

The total alkali, taken as NaOH, required in the overall process will generally not exceed 25% of the original dry weight of the substrate.

Upon completion of the alkaline peroxide treatment step, the insoluble cellulosic fiber product is separated from the aqueous alkaline phase, washed with water one or more times to remove alkali metal base and water-soluble compounds, acidified to pH 2-3 with any aqueous mineral acid or organic acid that is non-toxic, such as hydrochloric, nitric, sulfuric, citric, tartaric and acetic acid, rewashed with water until the pH of the filtrate water is greater than 5.5 and, if desired, dried.

The separated product can be dried in a conventional drier such as a rotary drier, a fluid bed drier, a pan drier or a spray drier. Alternatively, the product can be dewatered, for example, by pressing or centrifugation, prior to drying. Drying temperatures depend on the type of drier, but they should be high enough to efficiently dry, but low enough to avoid charring or darkening of the product. Preferably, product temperatures should not exceed 105°C.

The dried bleached substrate which results from the process of this invention can be ground for use as a dietary fiber for substitution for flour used to make cakes, breads, pasta, pizza and other baked goods, ice cream, yogurt, dietary fiber drinks, binding agents for processed meat and pharmaceutical tablets for human consumption.

Particularly in the case of a dietary fiber, the product of this invention is preferably fine ground by itself or co-ground with the regular flour with which it ultimately is to be mixed. Regular flour can be any flour such as wheat flour, corn flour, rice flour, rye flour or oat flour and need not be from the same plant as the original substrate. Co-grinding or milling with grains such as rice, corn, wheat, barley, oat, rye, etc. may be done after a preblending operation, to give a uniformly distributed mixture of regular flour and the dietary fiber flour of this invention.

The process of the invention is capable of producing dietary fibers

having low levels (in weight %) of proteins (less than 1), fatty substances (less than 0.01%) and ash-forming substances (less than 1.0%) including the siliceous material, taken as SiO_2 . The brightness value of the bleached product, as determined with a Hunter Color Difference Meter, Model D-2, which measures the dry product tamped flush with the rim of a round, 6 cm diameter x 1.8 cm deep metal can, is generally about 80 or more, but in the preferred cases will be higher than 90. In comparison, unbleached substrates typically have brightness values around 65 or they may be even lower. In addition, the bleached product consistently has a TDF content of generally over 90%.

10

EXAMPLE 1

Unground oat hulls weighing 281 grams with 11% moisture content were placed in a plastic bag along with 1969 grams of water and 200 grams of 5% NaOH solution. The ratio of pure NaOH versus. oat hulls (oven dry weight) was 4%. The bag was sealed by heat and placed in a 70° C water bath. At the end of one hour, the bag was taken out and opened. The NaOH extract was separated from the oat hulls by filtration. The filtered oat hulls were placed in a 2.8 liter pressure reactor. Three hundred grams of 5% NaOH solution were added to the hulls and the NaOH/starting hulls ratio was 6%. Water was added to the reactor until the total slurry weight became 1200 grams. The reactor was evacuated by a vacuum pump and pressurized with pure O_2 to 150 psig (1034 kPa). Then the reactor was placed inside an oven to be heated up to 120° C. It took about 90 minutes for the reactor to reach 120° C, and the inside temperature was kept at 120° C for 30 minutes. At the end of reaction, the reactor was taken out, cooled by immersing in cold water and degassed before opening. The oat hull slurry was filtered and the yield was about 60%.

The filtered oat hulls were placed inside the pressure reactor again. Three hundred grams of 5% NaOH were added to the hulls and the NaOH/starting hulls ratio was 6%. Water was added to the reactor until the total slurry weight became 1050 grams. The reactor was vacuumed and pressurized with pure O_2 to 150 psig (1034 kPa). It was placed into the oven to be heated up to 120° C. After the reactor was at 120° C for 30 minutes, it was taken out of the oven, cooled and degassed. The oat hull slurry was filtered and washed with 2 liters of water.

A portion of the washed oat hulls were placed inside a plastic bag. Solutions of NaOH, Na_2SiO_3 and H_2O_2 and water were added to the bag. Water was added to the bag until the oven dry weight of oat hulls versus the weight of the

slurry equalled 0.12. The ratios of NaOH, Na_2SiO_3 and H_2O_2 versus the oven dry weight of the washed hulls were 1% (w/w), 3% and 3% respectively. The bag was placed in the water bath at 70° C for 16 hours. Then the oat hull slurry was filtered, washed and acidified to pH 2.5 for 15 minutes. The acidified oat hulls were washed
5 till the pH of the filtrate was greater than 5.5. The wet hulls were dried in a lab fluid-bed dryer at 70° C for 20 minutes. The yield was 46.3%. The dried hulls were ground in a Willy mill to pass through the 20 mesh screen. The ground hulls had a brightness of 90.2, a water absorbency of 7.2 g/g and an oil absorbency of 6.6 cc/g.

10

EXAMPLE 2

Unground oat hulls weighing 112.4 grams with 11% moisture content were placed in a plastic bag along with 807.6 grams of water and 80 g of 5% NaOH solution. The ratio of pure NaOH versus oat hulls (oven dry weight) was 4%. The bag was sealed by heat and placed in a 70° C water bath. At the end of one hour,
15 the bag was taken out and opened. The NaOH extract was separated from the oat hulls by filtration. The filtered oat hulls were placed in a 2.8 liter pressure reactor. One hundred twenty grams of 5% NaOH solution were added to the reactor and water was added until the total slurry weight became 800 grams. It was approximately a 11.6% slurry. The reactor was evacuated by a vacuum pump and
20 pressurized with pure O_2 to 150 psig (1034 kPa). Then the reactor was placed inside an oven and heated up to 120° C. It took about 90 minutes for the reactor to reach 120° C and the inside temperature was kept at 120° C for 30 minutes. At the end of the reaction, the reactor was taken out of the oven, cooled and degassed before opening. The oat hull slurry was filtered and the yield was about 61.3%.

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The filtered oat hulls were placed inside the pressure reactor again. One hundred twenty grams of 5% NaOH were added to the hulls until the total slurry weight became 600 grams. The reactor was vacuumed and pressurized with pure O_2 to 150 psig (1034 kPa). It was placed in an oven and heated up to 120° C. After the reactor was at 120° C for 30 minutes, it was taken out of the oven, cooled
30 and degassed. The oat hull slurry was filtered, washed with 2 liters of water, and acidified to pH 2.5 for 15 minutes. The acidified oat hulls were washed twice with 500 ml of water. The wet hulls were dried in a lab fluid-bed dryer at 70° C for 20 minutes. The yield was 43.6%. The dried hulls were ground in a Willy mill to pass through a 20-mesh screen. The ground hulls had a brightness of 88.5, an ash content
35 of 1.11 wt. %, a water absorbency of 5.9 g/g and an oil absorbency of 4.9 cc/g.

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EXAMPLE 3

Unground oat hulls weighing 112.4 grams with 11% moisture content were placed in a plastic bag along with 807.6 grams of water and 80 grams of 5% NaOH solution. The ratio of pure NaOH versus oat hulls was 4%. The bag was sealed by heat and placed in a 70° C water bath. At the end of one hour, the bag was taken out and opened. The NaOH extract was separated from the oat hulls by filtration. The filtered oat hulls were placed in a 2.8 liter pressure reactor. One hundred twenty grams of 5% NaOH solution were added to the hulls and the NaOH/starting hulls ratio was 6%. Water was added to the reactor until the total slurry weight became 800 grams. It was approximately a 11.6% slurry. The reactor was evacuated by vacuum pump and pressurized with pure O₂ to 150 psig (1034 kPa). The reactor was placed inside an oven and heated up to 120° C for 30 minutes. At the end of the reaction, the reactor was taken out, cooled and degassed before opening. The oat hull slurry was filtered and the yield was about 61.3%.

The washed oat hulls were placed inside a plastic bag. Solutions of H₂O₂ and H₂SO₄ were added to the bag. The ratios of H₂O₂ and H₂SO₄ versus the oven dry weight of the washed hulls were 1% (w/w) and 2% (w/w) respectively. The total slurry weight was 1150 grams. The bag was placed in a water bath at 70° C for 60 minutes. Then the oat hull slurry was filtered and washed.

The filtered oat hulls were placed inside a 2.8 liter pressure reactor. One hundred twenty grams of 5% NaOH were added to the hulls and the NaOH/starting hulls ratio was 6%. Water was added to the reactor until the total slurry weight became 600 grams. The reactor was vacuumed and pressurized with pure O₂ to 150 psig (1034 kPa). It was placed in an oven and heated to 120° C. After the reactor was at 120° C for 30 minutes, it was taken out, cooled and degassed. The oat hull slurry was filtered, washed with 2 liters of water, and acidified to pH 2.5 for 15 minutes. The acidified hulls were washed twice with 500 ml of water. The wet hulls were dried in a lab fluid-bed dryer at 70° C for 20 minutes. The yield was 48.0%. The dried hulls were ground in a Willy mill to pass through a 20-mesh screen. The ground hulls had a brightness of 87.9, an ash content of 0.35%, a water absorbency of 5.7 g/g and an oil absorbency of 4.3 cc/g.

EXAMPLE 4

Unground oat hulls weighing 112.4 grams with 11% moisture content were placed in a plastic bag along with 187.6 grams of water and 200 grams of 5% NaOH solution. The ratio of pure NaOH versus oat hulls (oven dry weight) was

10%. The bag was sealed by heat and placed in a 90° C water bath. At the end of one hour, the bag was taken out and opened. The NaOH extract was separated from the oat hulls by filtration. The filtered oat hulls were placed in a 2.8 liter pressure reactor. One hundred twenty grams of 5% NaOH solution were added to the hulls and the NaOH/starting hulls ratio was 6%. Water was added to the reactor until the total slurry weight became 760 grams. The reactor was evacuated by a vacuum pump and pressurized with pure O₂ to 150 psig (1034 kPa). Then the reactor was placed inside an oven and heated up to 120° C. It took about 90 minutes for the reactor to reach 120° C, and the temperature inside the reactor was kept at 120° C for 30 minutes. At the end of the reaction, the reactor was taken out, cooled and degassed before opening. The oat hull slurry was filtered, washed with 2 liters of water, and acidified to pH 2.5 for 15 minutes. The acidified oat hulls were washed twice with 500 ml of water. The wet hulls were dried in a lab fluid-bed dryer at 70° C for 20 minutes. The yield was 70%. The dried hulls were ground in a Willy mill to pass through a 20-mesh screen. The ground hulls had a brightness of 80.9, an ash content of 0.76%, a water absorbency of 4.2 g/g and an oil absorbency of 2.9 cc/g.

EXAMPLE 5

Unground oat hulls weighing 112.4 grams with 11% moisture content were placed in a plastic bag along with 187.6 grams of water and 200 grams of 5% NaOH solution. The ratio of pure NaOH versus oat hulls (oven dry weight) was 10%. The bag was sealed by heat and placed in a 90° C water bath. At the end of one hour, the bag was taken out and opened. The NaOH extract was separated from the oat hulls by filtration. The filtered oat hulls were placed in a 2.8 liter pressure reactor. One hundred twenty grams of 5% NaOH solution were added to the hulls and the NaOH/starting hulls ratio was 6%. Water was added to the reactor until the total slurry weight became 762 grams. The reactor was evacuated by a vacuum pump and pressurized with pure O₂ to 150 psig (1034 kPa). Then the reactor was placed inside an oven and heated up to 120° C. It took about 90 minutes for the reactor to reach 120° C, and the temperature inside the reactor was kept at 120° C for 30 minutes. At the end of the reaction, the reactor was taken out, cooled and degassed before opening. The oat hull slurry was filtered, washed with 2 liters of water and the yield was about 70%.

The washed oat hulls were placed inside a plastic bag. Solutions of NaOH, H₂O₂ and Na₂SiO₃ and water were added to the bag. The ratios of NaOH, H₂O₂ and Na₂SiO₃ versus the oven dry weight of the oat hulls were 1%, 1% and

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3% respectively. The total slurry weight was 700 grams. The bag was placed in a water bath at 70° C for 3 hours. Then the oat hull slurry was filtered, washed and acidified to pH 2.5 for 15 minutes. The acidified oat hulls were washed twice with 500 ml of water.

5 The wet hulls were dried in a lab fluid-bed dryer at 70° C for 20 minutes. The yield was 67.1%. The dried hulls were ground in a Willy mill to pass through a 20-mesh screen. The ground hulls had a brightness of 84.6, an ash content of 0.58%, a water absorbency of 5.0 g/g and an oil absorbency of 3.3 cc/g.

10 EXAMPLE 6

 Unground oat hulls weighing 112.4 grams with 11% moisture content were placed in a plastic bag along with 807.6 grams of water and 80 g of 5% NaOH solution. The ratio of pure NaOH versus oat hulls (oven dry weight) was 4%. The bag was sealed by heat and placed in a 70° C water bath. At the end of one hour,
15 the bag was taken out and opened. The NaOH extract was separated from the oat hulls by filtration. The filtered oat hulls were placed in a 2.8 liter pressure reactor. One hundred twenty grams of 5% NaOH solution were added to the reactor and water was added until the total slurry weight became 800 grams. The reactor was evacuated by vacuum pump and pressurized with pure O₂ to 150 psig (1034 kPa).
20 Then the reactor was placed inside an oven and heated up to 120° C. It took about 90 minutes for the reactor to reach 120° C and the inside temperature was kept at 120° C for 30 minutes. At the end of the reaction, the reactor was taken out, cooled and degassed before opening. The oat hull slurry was filtered and the yield was about 61.3%.

25 The filtered oat hulls were placed inside the pressure reactor again. One hundred twenty grams of 5% NaOH and 3.3 grams of 30% hydrogen peroxide solution were added to the hulls and water was added until the total slurry weight became 600 grams. The reactor was vacuumed and pressurized with pure O₂ to 150 psig (1034 kPa). It was placed in an oven and heated to 120° C. After the reactor
30 was at 120° C for 30 minutes, it was taken out of the oven, cooled and degassed. The oat hull slurry was filtered, washed with 2 liters of water, and acidified to pH 2.5 for 15 minutes. The acidified hulls were washed twice with 500 ml of water. The wet hulls were dried in a lab fluid-bed dryer at 70° C for 20 minutes. The yield was 45.7%. The dried hulls were ground in a Willy mill to pass through a 20-mesh
35 screen. The ground hulls had a brightness of 90.1, an ash content of 0.98% wt, %, a water absorbency of 5.7 g/g and an oil absorbency of 4.5 cc/g.

EXAMPLE 7

Unground oat hulls weighing 281 grams with 11% moisture content were placed in a plastic bag along with 1969 grams of water and 200 grams of 5% NaOH solution. The ratio of pure NaOH versus oat hulls (oven dry weight) was 4%. The bag was sealed by heat and placed in a 70° C water bath. At the end of one hour, the bag was taken out and opened. The NaOH extract was separated from the oat hulls by filtration. The filtered oat hulls were placed in a 2.8 liter pressure reactor. Three hundred grams of 5% NaOH solution were added to the hulls and the NaOH/starting hulls ratio was 6%. Water was added to the reactor until the total slurry weight became 1200 grams. The reactor was evacuated by a vacuum pump and pressurized with pure O₂ to 150 psig (1034 kPa). Then the reactor was placed inside an oven to be heated up to 120° C. It took about 90 minutes for the reactor to reach 120° C, and the inside temperature was kept at 120° C for 30 minutes. At the end of reaction, the reactor was taken out, cooled and degassed before opening. The oat hull slurry was filtered and the yield was about 60%.

Then the oat hull slurry was reslurried and acidified by dilute HCl to pH 2.5 for 15 minutes. The acidified oat hulls were washed till the pH of the filtrate was greater than 5.5. The wet hulls were dried in a lab fluid-bed dryer at 70° C for 20 minutes. The dried hulls were ground in a Willy mill to pass through the 20-mesh screen. The ground hulls had a brightness of 68.2, a water absorbency of 4.3 g/g and an oil absorbency of 3.0 cc/g.

EXAMPLE 8

Unground oat hulls weighing 281 grams with 11% moisture content were placed in a plastic bag along with 1969 grams of water and 200 grams of 5% NaOH solution. The ratio of pure NaOH versus oat hulls (oven dry weight) was 4%. The bag was sealed by heat and placed in a 70° C water bath. At the end of one hour, the bag was taken out and opened. The NaOH extract was separated from the oat hulls by filtration. The filtered oat hulls were placed in a 2.8 liter pressure reactor. Three hundred grams of 5% NaOH solution were added to the hulls and the NaOH/starting hulls ratio was 6%. Water was added to the reactor until the total slurry weight became 1200 grams. The reactor was evacuated by a vacuum pump and pressurized with pure O₂ to 150 psig (1034 kPa). Then the reactor was placed inside an oven to be heated up to 120° C. It took about 90

minutes for the reactor to reach 120° C, and the inside temperature was kept at 120° C for 30 minutes. At the end of reaction, the reactor was taken out, cooled and degassed before opening. The oat hull slurry was filtered and the yield was about 60%.

5 The filtered oat hulls were placed inside the pressure reactor again. One hundred seventy-five grams of 5% NaOH were added to the hulls and the NaOH/starting hulls ratio was 3.5%. Water was added to the reactor until the total slurry weight became 1050 grams. The reactor was vacuumed and pressurized with pure O₂ to 150 psig (1034 kPa). It was placed into the oven to be heated up to
10 120° C. After the reactor was at 120° C for 30 minutes, it was taken out of the oven, cooled and degassed. The oat hull slurry was filtered and washed with 2 liters of water.

15 Then the wet oat hulls were reslurried and acidified by dilute HCl to pH 2.5 for 15 minutes. The acidified oat hulls were washed till the pH of the filtrate was greater than 5.5. The wet hulls were dried in a lab fluid-bed dryer at 70° C for 20 minutes. The yield was 51%. The dried hulls were ground in a Willy mill to pass through the 20-mesh screen. The ground hulls had a brightness of 83.5, a water absorbency of 5.0 g/g and an oil absorbency of 3.5 cc/g.

20

EXAMPLE 9

Unground oat hulls weighing 281 grams with 11% moisture content were placed in a plastic bag along with 1969 grams of water and 200 grams of 5% NaOH solution. The ratio of pure NaOH versus oat hulls (oven dry weight) was 4%. The bag was sealed by heat and placed in a 70° C water bath. At the end of
25 one hour, the bag was taken out and opened. The NaOH extract was separated from the oat hulls by filtration. The filtered oat hulls were placed in a 2.8 liter pressure reactor. Three hundred grams of 5% NaOH solution were added to the hulls and the NaOH/starting hulls ratio was 6%. Water was added to the reactor until the total slurry weight became 1200 grams. The reactor was evacuated by a
30 vacuum pump and pressurized with pure O₂ to 150 psig (1034 kPa). Then the reactor was placed inside an oven to be heated up to 120° C. It took about 90 minutes for the reactor to reach 120° C, and the inside temperature was kept at 120° C for 30 minutes. At the end of reaction, the reactor was taken out, cooled and degassed before opening. The oat hull slurry was filtered and the yield was about
35 60%.

The filtered oat hulls were placed inside the pressure reactor again. Two hundred twenty-five grams of 5% NaOH were added to the hulls and the NaOH/starting hulls ratio was 4.5%. Water was added to the reactor until the total slurry weight became 1050 grams. The reactor was vacuumed and pressurized with pure O₂ to 150 psig (1034 kPa). It was placed into the oven to be heated up to 120° C. After the reactor was at 120° C for 30 minutes, it was taken out of the oven, cooled and degassed. The oat hull slurry was filtered and washed with 2 liters of water.

Then the wet oat hulls were reslurried and acidified by dilute HCl to pH 2.5 for 15 minutes. The acidified oat hulls were washed till the pH of the filtrate was greater than 5.5. The wet hulls were dried in a lab fluid-bed dryer at 70° C for 20 minutes. The dried hulls were ground in a Willy mill to pass through the 20-mesh screen. The ground hulls had a brightness of 84.1, a water absorbency of 5.6 g/g and an oil absorbency of 5.2 cc/g.

EXAMPLE 10

Unground oat hulls weighing 281 grams with 11% moisture content were placed in a plastic bag along with 1969 grams of water and 200 grams of 5% NaOH solution. The ratio of pure NaOH versus oat hulls (oven dry weight) was 4%. The bag was sealed by heat and placed in a 70° C water bath. At the end of one hour, the bag was taken out and opened. The NaOH extract was separated from the oat hulls by filtration. The filtered oat hulls were placed in a 2.8 liter pressure reactor. Three hundred grams of 5% NaOH solution were added to the hulls and the NaOH/starting hulls ratio was 6%. Water was added to the reactor until the total slurry weight became 1200 grams. The reactor was evacuated by a vacuum pump and pressurized with pure O₂ to 150 psig (1034 kPa). Then the reactor was placed inside an oven to be heated up to 120° C. It took about 90 minutes for the reactor to reach 120° C, and the inside temperature was kept at 120° C for 30 minutes. At the end of reaction, the reactor was taken out, cooled and degassed before opening. The oat hull slurry was filtered and the yield was about 60%.

The filtered oat hulls were placed inside the pressure reactor again. Three hundred grams of 5% NaOH were added to the hulls and the NaOH/starting hulls ratio was 6%. Water was added to the reactor until the total slurry weight became 1050 grams. The reactor was vacuumed and pressurized with pure O₂ to 150 psig (1034 kPa). It was placed into the oven to be heated up to 120° C. After

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the reactor was at 120° C for 30 minutes, it was taken out of the oven, cooled and degassed. The oat hull slurry was filtered and washed with 2 liters of water.

A portion of the washed oat hulls was placed inside a plastic bag. A 10% peracetic acid solution was added to the oat hulls and the ratio of pure peracetic acid to the oven dry weight of the wet hulls was 2%. Water was also added to the bag until the ratio of the oven dry weight hulls versus the liquid was 10%. The bag was sealed by heat and placed in a water bath at 70° C for one hour. The oat hull slurry was filtered and washed with water.

The washed oat hulls were placed inside a plastic bag. Solutions of NaOH, Na_2SiO_3 and H_2O_2 and water were added to the bag. Water was added to the bag until the oven dry weight of oat hulls versus the weight of the slurry equalled 0.12. The ratios of NaOH, Na_2SiO_3 and H_2O_2 versus the oven dry weight of the washed hulls were 1% (w/w), 3% and 2% respectively. The bag was placed in the water bath at 70° C for 3 hours. Then the oat hull slurry was filtered, washed and acidified to pH 2.5 for 15 minutes. The acidified oat hulls were washed till the pH of the filtrate was greater than 5.5. The wet hulls were dried in a lab fluid-bed dryer at 70° C for 20 minutes. The yield was about 46%. The dried hulls were ground in a Willy mill to pass through a 20 mesh screen. The ground hulls had a brightness of 90.8, a water absorbency of 7.2 g/g and an oil absorbency of 6.5 cc/g.

EXAMPLE 11

Unground oat hulls weighing 281 grams with 11% moisture content were placed in a 2.8 liter pressure reactor. Three hundred grams of 5% NaOH solution were added to the hulls and the NaOH/starting hulls ratio was 6%. Water was added to the reactor until the total slurry weight became 1751 grams. The reactor was evacuated by a vacuum pump and pressurized with pure O_2 to 150 psig (1034 kPa). Then the reactor was placed inside an oven to be heated up to 120° C. It took about 90 minutes for the reactor to reach 120° C, and the inside temperature was kept at 120° C for 30 minutes. At the end of the reaction, the reactor was taken out, cooled and degassed before opening. The oat hull slurry was filtered and the yield was about 74.7%.

Then a portion of the wet oat hulls were washed and acidified by dilute HCl to pH 2.5 for 15 minutes. The acidified oat hulls were washed with 500 ml of water twice. The wet hulls were dried in a lab fluid-bed dryer at 70° C for 20 minutes. The dried hulls were ground in a Willy mill to pass through the 20 mesh screen. The ground hulls had a brightness of 61.0, a water absorbency of 3.4 g/g and

an oil absorbency of 2.5 cc/g.

EXAMPLE 12

5 Uground oat hulls weighing 33.6 grams with 10.7% moisture content
were placed in a pressure reactor along with 10.3 grams of 35% NaOH solution, 4.8
grams of 37.6% sodium silicate solution, 4.4 grams of 13.5% sodium
tripolyphosphate solution, 6.2 grams of 29.2% H_2O_2 solution and 240 grams of
potable water. The ratios of NaOH, Na_2SiO_3 , $Na_5P_3O_{10}$ and H_2O_2 versus oat
hulls (oven dry weight) were 12%, 6%, 2% and 6%. The reactor was pressurized
10 with 30 psig O_2 and heated up to 80° C. The reaction was under 30 psig O_2 for 60
minutes.

At the end of one hour, the reactor was vented and the content was
taken out. The oat hull slurry (Gap in text) #1 filter paper. The wet hulls were
washed with 300 ml of water twice and reslurried to 300 grams with water. The
15 slurry was acidified to pH 2.2 with 2.5 grams of 10% HCl and was stirred for 15
minutes. It was then filtered, washed with 300 ml of water twice and dried in a
fluidized bed dryer at 70° C for 20 minutes. The yield was 54.8%. The dried hulls
were ground in a Willy mill to pass a 20 mesh screen. The ground hulls had a
brightness of 85.5, a water absorbency of 7.0 g/g and an oil absorbency of 5.6 cc/g.

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CLAIMS:

1. A process for preparing low calorie cellulosic dietary fiber from a nonwoody agricultural residue comprising providing an aqueous slurry of 5 to 35 weight percent of said residue or a mixture of such residues, containing dissolved therein 1 to 20 weight percent, based on dry residue, of a base, in a pressure vessel, pressurizing said vessel to 20 to 300 pounds per square inch guage with oxygen and heating the slurry to from 50° to 150°C for 5 to 180 minutes to provide a delignified cellulosic dietary fiber slurry and a lignin containing extract solution and separating said delignified cellulosic dietary fiber from said lignin containing extract solution, forming said dietary fiber into a second aqueous slurry containing from 5 to 35 weight percent of dietary fiber and having dissolved therein from 1 to 20 weight percent, based on said fiber, of a base, in a pressure vessel, and pressuring said vessel to from 20 to 300 pounds per square inch guage with oxygen and heating the slurry to from 50° to 150°C for 5 to 180 minutes.

2. The process of Claim 1 wherein the nonwoody lignocellulosic substrate is first treated with an aqueous basic solution containing 1 to 20 weight percent base, based on dry weight of the substrate, at a temperature to 20° to 100°C for 5 to 180 minutes and the substrate separated from the extract prior to treatment with oxygen.

3. The process of Claim 2 wherein the substrate after one of the two oxygenation steps is heated with an aqueous bleaching solution.

4. The process of Claim 3 wherein the oxygenation in both oxygenation steps is carried out at 50 to 200 pounds per square inch gauge.

5 5. The process of Claim 4 wherein both oxygenation steps are carried out at 90° to 130°C.

6. The process of Claim 5 wherein both oxygenation steps are performed for from 30 to 90 minutes.
10

7. The process of Claim 6 wherein the bleaching step is performed using an alkaline hydrogen peroxide solution.

15 8. The process of Claim 7 wherein the substrate is a cereal grain hull.

9. The process of Claim 1 wherein at least one of the oxygenation steps is carried out in the presence of 0.5
20 to 10 percent by weight, based on dry substrate, of a peroxide.

10. The process of Claim 9 wherein the nonwoody lignocellulosic substrate is first treated with an aqueous
25 basic solution containing 1 to 20 weight percent base, based on dry weight of the substrate, at a temperature of 20° to 100°C for 5 to 180 minutes and the substrate separated from the extract prior to the first treatment with oxygen.

30 11. The process of Claim 10 wherein both oxygenation steps are carried out at 50 to 200 pounds per square inch gauge.

12. The process of Claim 11 wherein both
35 oxygenation steps are carried out at 90° to 130°C.

13. The process of Claim 12 wherein both oxygenation steps are performed for from 30 to 90 minutes.

14. The process of Claim 13 wherein the substrate
5 is a cereal grain hull.





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(21) International Application Number: PCT/US91/08147 (22) International Filing Date: 8 November 1991 (08.11.91) (30) Priority data: 616,124 20 November 1990 (20.11.90) US (71) Applicant: E.I. DU PONT DE NEMOURS AND COMPANY [US/US]; 1007 Market Street, Wilmington, DE 19898 (US). (72) Inventors: CHANG, Hou-Min ; 3410 Redbud Lane, Raleigh, NC 27607 (US). CHIN, Yung-Chang ; 3F Number 15, Alley 6, Lane 324, Chung-ho Road, Chung-ho City, Taipei (TW). CHOU, Yu-Chia, Terry ; 27510 Valley Run Drive, Wilmington, DE 19810 (US).		(74) Agents: KRUKIEL, Charles, E. et al., E.I. du Pont de Nemours and Company, Legal Patent Records Center, 1007 Market Street, Wilmington, DE 19898 (US). (81) Designated States: AT (European patent), AU, BB, BE (European patent), BF (OAPI patent), BG, BJ (OAPI patent), BR, CA, CF (OAPI patent), CG (OAPI patent), CH (European patent), CI (OAPI patent), CM (OAPI patent), CS, DE (European patent), DK (European patent), ES (European patent), FI, FR (European patent), GA (OAPI patent), GB (European patent), GN (OAPI patent), GR (European patent), HU, IT (European patent), JP, KP, KR, LK, LU (European patent), MC, MG, ML (OAPI patent), MN, MR (OAPI patent), MW, NL (European patent), NO, PL, RO, SD, SE (European patent), SN (OAPI patent), SU*, TD (OAPI patent), TG (OAPI patent). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i> (88) Date of publication of the international search report: 26 November 1992 (26.11.92)
(54) Title: METHOD FOR PRODUCING DIETARY FIBERS FROM NONWOODY LIGNOCELLULOSIC SUBSTRATES BY OXIDATION		
(57) Abstract <p>A process for delignifying and optionally bleaching nonwoody lignocellulosic substrates to produce a dietary fiber suitable for human consumption is disclosed. The process involves (a) an optional first step of treating the substrate with an aqueous alkali solution containing 1 to 20 % by weight, based on dry substrate, of a base at 20° to 100 °C to swell and remove base soluble materials from the substrate; (b) separating the substrate and optionally washing it with water; (c) uniformly wetting the substrate with an aqueous alkaline solution containing 1 to 20 wt. % of base, based on dry substrate, to form a slurry, placing the slurry in a pressure vessel which is pressured with oxygen gas to 20 to 300 psig (138 to 2070 kPa) for 5 to 180 minutes at a temperature of 50° to 150 °C to delignify the substrate, separating the delignified substrate from the lignin containing extract solution; (d) optionally bleaching the delignified substrate, preferably with an alkaline aqueous hydrogen peroxide solution; and (e) recovering the delignified substrate. Optionally more than one oxygenation step can be used with the substrate being separated from the oxygenation-extraction medium between oxygenation steps. Optionally, in a preferred aspect of the present invention a peroxide, preferably 0.5 to 10 weight percent hydrogen peroxide, is included in the reaction medium during one of the oxygenation steps.</p>		

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It is under examination in which parts of the former Soviet Union the designation of the Soviet Union has effect.

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INTERNATIONAL SEARCH REPORT

International Application No.

PCT/US 91/08147

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) ⁶		
According to International Patent Classification (IPC) or to both National Classification and IPC		
Int.Cl. 5 D21C5/00;	D21C3/02;	D21C3/26; A23K1/12
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
Int.Cl. 5	D21C ; A23K	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹		
Category *	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
X	US,A,4 087 316 (COTTON INCORPORATED) 2 May 1978 see column 7, line 51 - column 8, line 59 see column 9, line 5 - line 14 ---	1,2,4,5
Y	AU,A,451 395 (ASSOCIATED PULP AND PAPER MILLS LIMITED) 8 August 1974 see page 6, line 2 - line 19; claims ---	1-29
Y	US,A,4 842 877 (XYLAN INC.) 27 June 1989 see column 8, line 33 - line 38; claims ---	1-29
A	EP,A,0 337 653 (E. I. DU PONT DE NEMOURS AND COMPANY) 18 October 1989 see the whole document ---	1-3,7-9, 18,19,23
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IV. CERTIFICATION		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
27 MARCH 1992	02.11.92	
International Searching Authority	Signature of Authorized Officer	
EUROPEAN PATENT OFFICE	BERNARDO NORIEGA F. <i>J. Bernasch</i>	

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ANNEX TO THE INTERNATIONAL SEARCH REPORT
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